

## CLAIMS

- 1) Process for desulfurizing hydrocarbons which boil within the range of 35° to 250°C, containing olefins and more than 150 ppm of sulfur , with possible skeleton isomerization of olefins, using a catalyst which comprises a metal of group VIII, a metal of group VI, a metal oxide as carrier and a component A selected from:
- a) zeolite belonging to the FER type, in a quantity ranging from 5 to 30% by weight with respect to the total weight of the catalyst,
  - b) phosphorous in a quantity ranging from 0.1 to 10 % weight with respect to the total weight of the catalyst,
  - c) mixtures thereof,
- where when the component A is only phosphorous either the catalyst is obtained by impregnation of the metal oxide carrier with an aqueous solution of  $H_3PO_4$  followed by impregnation with an aqueous solution of the metal of group VIII and an aqueous solution of the metal of group VI, or the catalyst is obtained by drying and calcination of a gel obtained mixing an alcohol

dispersion containing a soluble salt of the metal of group VIII and an organic source of aluminum with an aqueous solution containing a soluble salt of the metal of group VI and  $H_3PO_4$ , or the catalyst is obtained by impregnation with an aqueous solution of  $H_3PO_4$  of a gel, dried and calcined, obtained mixing an alcohol dispersion containing a soluble salt of the metal of group VIII and an organic source of aluminum with an aqueous solution containing a soluble salt of the metal of group VI.

2) Process according to claim 1 for desulfurizing hydrocarbons which boil within the range of  $35^\circ$  to  $250^\circ C$ , containing olefins and more than 150 ppm of sulfur, with skeleton isomerization of olefins, using a catalyst comprising a metal of group VIII, a metal of group VI, a metal oxide as carrier, and a component A selected from a zeolite belonging to the FER type, in a quantity ranging from 5 to 30% by weight with respect to the total weight of the catalyst, and mixtures of said zeolite of FER type in a quantity ranging from 5 to 30% by weight with respect to the total weight of the catalyst, with phosphorous in a quantity ranging

from 0.1 to 10 % weight with respect to the total weight of the catalyst.

A 3) The process according to claim 1 ~~or 2~~ wherein the metal of group VIII is selected from Cobalt, Nickel and their mixtures.

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A 4) The process according to claim 1 ~~or 2~~ wherein the metal of group VI is selected from molybdenum, tungsten and their mixtures.

CLAIM 3

A 5) The process according to ~~claims 3 and 4~~ wherein the metal of group VIII is cobalt and the metal of group VI is molybdenum.

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6) The process according to claim 1 ~~or 2~~ wherein the weight percentage of metal of group VIII varies from 1 to 10% with respect to the total weight of the catalyst.

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7) The process according to claim 6 wherein the weight percentage of metal of group VIII varies from 2 to 6%.

A 8) The process according to claim 1 ~~or 2~~ wherein the weight percentage of metal of group VI varies from 4 to 20% with respect to the total weight of the catalyst.

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9) The process according to claim 8 wherein the weight percentage of metal of group VI varies from 8 to 13 %.

## CLAIM 6

10) The process according to ~~claims 6 and 8~~ wherein the molar ratio between the metal of group VIII and the metal of group VI is less than or equal to 2.

11) The process according to claim 10 wherein the molar ratio between the metal of group VIII and the metal of group VI is less than or equal to 1.

12) The process according to claim 1 ~~or 2~~ wherein the metal oxide used as carrier is selected from silica, alumina, silico-aluminas, titania, zirconia and mixtures of thereof.

13) The process according to claim 12, wherein the metal oxide is alumina.

14) The process according to claim 1 ~~or 2~~ wherein the catalyst comprises a zeolite of FER type selected from Ferrierite, FU-9, ISI-6, Nu-23, Sr-D, ZSM-35.

15) The process according to claim 14 wherein the zeolite is ZSM-35.

16) The process according to claim 1, ~~2, 14 or 15~~ wherein the zeolite of FER type is in the form in which the cation sites are prevalently occupied by hydrogen ions.

17) The process according to claim 16, wherein at least 80% of the cation sites is occupied by hydrogen ions.

18) The process according to claim 1, ~~2, 14 or 15~~ wherein the zeolite has Si/Al ratio < 20.

5 19) The process according to claim 1 ~~or 2~~ wherein the catalyst contains zeolite of FER type as component A, and is prepared as follows:

10 a) an alcohol dispersion is prepared, containing a soluble salt of the metal of group VIII, the zeolite of the FER type and an organic source of aluminum;

b) an aqueous solution is prepared, containing a soluble salt of the metal of group VI and optionally formamide;

15 c) the alcohol dispersion and the aqueous solution are mixed, obtaining a gel;

d) aging of the gel at a temperature ranging from 10 to 40°C;

e) drying of the gel;

f) calcination of the gel.

20 20) The process according to claim 19, wherein in step

a) the metal salt of group VIII is nitrate.

21) The process according to claim 19 wherein the organic source of aluminum is aluminum-trialkoxide having the formula  $(RO)_3Al$ , wherein R is isopropyl or sec-butyl.

5 22) The process according to claim 19 wherein in step b) the soluble salt of the metal of group VI is an ammonium salt.

10 23) The process according to claim 19 wherein step e) is carried out at a temperature ranging from 80 to 120°C.

24) The process according to claim 19, wherein step f) is carried out at a temperature ranging from 400 to 600°C.

15 25) The process according to claim 1 ~~or 2~~, wherein the catalyst contains a zeolite of FER type as component A, and is prepared by:

a) impregnation of metal oxide carrier with an aqueous solution of metal of group VIII and an aqueous solution of metal of group VI,

20 b) drying and calcination of the material resulting from step a)

c) mixing the impregnated metal oxide obtained from step b) with the zeolite of FER type.

26) The process according to claim 25 wherein the impregnated metal oxide from step b) is crushed and sieved in particles of  $<0.2$  mm before the mixing in step c).

27) The process according to claim 26 wherein in the step c) metal oxide particles and zeolite of FER type are dispersed in an organic solvent, then the solvent is vaporized and the so obtained catalyst is dried and calcined.

28) The process according to claim 26 wherein in step c) metal oxide particles and zeolite of FER type are mixed in the presence of a binder and optionally of a combustible organic polymer, to obtain a mixture which is kneaded with a peptizing acid solution, extruded, dried and calcined, or pelletized, dried and calcined.

29) The process according to claim 1 ~~or 2~~ wherein the catalyst contains phosphorous in a quantity ranging from 1 to 5 % wt with respect to the total weight of the catalyst.

30) The process according to claim 1 wherein the catalyst contains phosphorous as component A and is prepared by impregnation of the metal oxide carrier with an aqueous solution of  $H_3PO_4$  followed by impregnation with an aqueous solution of the metal of group VIII and an aqueous solution of the metal of group VI, wherein the metal oxide carrier has a surface area lower than  $240 \text{ m}^2/\text{g}$ .

31) The process according to claim 1 ~~or 2~~ carried out at a temperature ranging from  $220$  to  $340^\circ\text{C}$ , at a pressure ranging from  $5$  to  $20 \text{ Kg/cm}^2$ , at a LHSV ranging from  $1$  to  $10 \text{ h}^{-1}$  in the presence of hydrogen in a quantity ranging from  $100$  to  $500$  times with respect to the hydrocarbons present ( $\text{Nl/l}$ ).

~~32) A catalyst containing a metal of group VIII, a metal of group VI, a metal oxide as carrier and a zeolite belonging to the FER type, in a quantity ranging from  $5$  to  $30\%$  by weight with respect to the total weight of the catalyst, prepared as follows:~~

~~a) an alcohol dispersion is prepared, containing a soluble salt of the metal of group VIII, the zeolite of the FER group and an organic source of Aluminum;~~



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~~aqueous solution containing a soluble salt of the metal~~  
of group VI.

41) The catalyst according to claim 38, 39 or 40  
containing phosphorous in a quantity ranging from 1 to  
5 5 % wt with respect to the total weight of the  
~~catalyst.~~

A 32 ~~42~~) The process according to claim 1 ~~or 2~~ wherein the  
hydrocarbons boiling within the range of 35 to 250°C  
contain more than 1000 ppm of S.

A 10 33 ~~43~~) The process according to claim 1 ~~or 2~~ wherein  
hydrocarbons boiling within the range of 35 to 250°C  
derive from cracking processes.

34 ~~44~~) The process according to claim 1 ~~or 2~~ wherein the  
catalyst is in extruded form.

15 35 ~~45~~) The process according to claim 31 carried out at a  
temperature ranging from 220 to 330°C.

36 32) A catalyst containing a metal of group VIII, a  
metal of group VI, a metal oxide as carrier and a  
zeolite belonging to the FER type, in a quantity  
ranging from 5 to 30% by weight with respect to the  
total weight of the catalyst, prepared as follows:

a) an alcohol dispersion is prepared, containing a  
soluble salt of the metal of group VIII, the zeolite of  
the FER group and an organic source of Aluminum;

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b) an aqueous solution is prepared, containing a soluble salt of the metal of group VI and optionally formamide;

c) the alcohol dispersion and the aqueous solution are mixed, obtaining a gel;

d) aging of the gel at a temperature ranging from 10 to 40°C;

e) drying of the gel;

f) calcination of the gel.

37. A catalyst according to claim 36, wherein said catalyst has a surface area greater than 300 m<sup>2</sup>/g.

38 ~~37~~) A catalyst which comprise a metal of group VIII, a metal of group VI, a metal oxide as carrier, a zeolite of the FER type, in a quantity ranging from 5 to 30% by weight with respect to the total weight of the catalyst, and phosphorous in a quantity ranging from 0.1 to 10%.

38 ~~37~~) The catalyst according to claim ~~38~~ <sup>38</sup> containing phosphorous in a quantity ranging from 1 to 5 % wt with respect to the total weight of the catalyst.

40 ~~34)~~ A process for preparing the catalyst of claim <sup>38</sup>~~38~~  
comprising the following steps:

5 a) an alcohol dispersion is prepared, containing a  
soluble salt of the metal of group VIII, the zeolite of  
FER type and an organic source of aluminum;

b) an aqueous solution is prepared, containing a  
soluble salt of the metal of group VI,  $H_3PO_4$  and  
optionally formamide;

10 c) the alcohol dispersion and the aqueous solution are  
mixed, obtaining a gel;

d) aging of the gel at a temperature ranging from 10 to  
40°C;

e) drying of the gel;

f) calcination of the gel.

15 41 ~~35)~~ A process for preparing the catalyst of claim <sup>38</sup>~~38~~  
comprising the following steps:

a) an alcohol dispersion is prepared, containing a  
soluble salt of the metal of group VIII, a zeolite of  
FER type and an organic source of aluminum;

20 b) an aqueous solution is prepared, containing a  
soluble salt of the metal of group VI, and optionally  
formamide;

c) the alcohol dispersion and the aqueous solution are mixed, obtaining a gel;

d) aging of the gel at a temperature ranging from 10 to 40°C;

5 e) drying of the gel;

f) calcination of the gel.

g) impregnation of the catalyst obtained from step f) with an aqueous solution of  $H_3PO_4$ , drying and calcination.

10 ~~42~~<sup>36</sup> Process for preparing the catalyst of claim ~~37~~<sup>38</sup> comprising:

a) impregnation of metal oxide with an aqueous solution of  $H_3PO_4$ , drying and calcination,

15 b) impregnation of the material resulting from step a) with an aqueous solution of metal of group VIII and an aqueous solution of metal of group VI,

c) drying and calcination of the material resulting from step b)

20 d) mixing the impregnated metal oxide obtained from step c) with the zeolite of FER type.

43 ~~38~~ A catalyst which comprises a metal of group VIII, a metal of group VI, a metal oxide as carrier and P in a quantity ranging from 0.1 to 10 % weight with respect to the total weight of the catalyst, prepared by

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impregnation of the metal oxide carrier with an aqueous solution of  $H_3PO_4$  followed by impregnation with an aqueous solution of the metal of group VIII and an aqueous solution of the metal of group VI.

- 5 ~~44~~ 39) A catalyst which comprises a metal of group VIII, a metal of group VI, a metal oxide as carrier and P in a quantity ranging from 0.1 to 10 % weight with respect to the total weight of the catalyst, prepared by drying and calcination of a gel obtained mixing an alcohol
- 10 dispersion containing a soluble salt of the metal of group VIII and an organic source of aluminum with an aqueous solution containing a soluble salt of the metal of group VI and  $H_3PO_4$ .

- 15 ~~45~~ 40) A catalyst which comprises a metal of group VIII, a metal of group VI, a metal oxide as carrier and P in a quantity ranging from 0.1 to 10 % weight with respect to the total weight of the catalyst, prepared by impregnation with an aqueous solution of  $H_3PO_4$  of a gel, dried and calcined, obtained mixing an alcohol
- 20 dispersion containing a soluble salt of the metal of group VIII and an organic source of aluminum with an

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aqueous solution containing a soluble salt of the metal of group VI.

4641) The catalyst according to claim ~~38~~<sup>43</sup>, ~~39~~<sup>44</sup> or ~~40~~<sup>45</sup> containing phosphorous in a quantity ranging from 1 to 5 % wt with respect to the total weight of the catalyst.

~~42) The process according to claim 1 or 2 wherein the hydrocarbons boiling within the range of 35 to 250°C contain more than 1000 ppm of S.~~

43) The process according to claim 1 or 2 wherein hydrocarbons boiling within the range of 35 to 250°C derive from cracking processes.

44) The process according to claim 1 or 2 wherein the catalyst is in extruded form.

45) The process according to claim 31 carried out at a temperature ranging from 220 to 330°C.

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